# Monoterpenes of *Gutierrezia sarothrae*

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The 11 major monoterpene components of *Gutierrezia sarothrae* were isolated and identified by spectral methods and comparison with authentic samples. α-Pinene (1), β-pinene (2), and limonene (3) were found to comprise 47.9–74.7% of the oils from whole green plant extracts, with six bicyclic alcohols and two bicyclic ketones comprising 3.3–40.8% of the oils. The variation in the ratio of components contained within the oils was shown to be a seasonal occurrence, with greater quantities of 1–3 present in the spring. The components identified in this study are not in agreement with previously published reports. The differences between reports are likely the result of subspecies variation.

The investigation of the monoterpenes of *Gutierrezia sarothrae* was initially undertaken in an effort to obtain geraniol from a nontraditional biological source, as *G. sarothrae* was reported to contain significant quantities of geraniol (Table I). *G. sarothrae* is alternately known as broom snakeweed, broomweed, matchweed, turpentine-weed, and yellow top (*Range Plant Handbook*, 1937). It is a resinous half-shrub with woody roots, crowns, and stembases and is widely distributed over the western states, ranging from Alberta to Manitoba, western Texas, southern California, Nevada, and Idaho (*Range Plant Handbook*, 1937). It occurs principally on the plains, in semidesert valleys, on low-lying foothills, and on mountain slopes, at elevations of 4000–8000 ft above sea level (*Range Plant Handbook*, 1937).

*G. sarothrae* is reported to be toxic to range animals, causing abortions or death in some cases (Kingsbury, 1964), but its effects appear to be variable, as livestock often graze without adverse effects (*Range Plant Handbook*, 1937). The poisonous principle has not been identified, but a saponin has been reported to be the cause (Kingsbury, 1964). Alternately, selenium may be the active agent as *G. sarothrae* is known to be a faculative selenium absorber (Kingsbury, 1964).

## RESULTS AND DISCUSSION

A sample of *G. sarothrae* was initially collected in October 1983 in Muskrat Canyon, UT (specimen voucher on file at the Garrett Herbarium, University of Utah). The green stems, leaves, and flowers were separated from the woody portions of the plant and the whole green plant (stem, leaves, flowers) extracted with pentanes. The extracts were then nonequilibrium distilled to give oils for further analysis.

The 11 major components present in the whole green plant oil were isolated by a combination of MPLC and preparative GLC (Chart I). These 11 components were identified by $^1$H NMR, IR, and MS and compared to authentic commercially available samples (α-pinene (1), β-pinene (2), limonene (3)) or samples synthesized from 1 (Scheme I), 2 (Scheme II), or borneol by literature procedures (Whitham, 1961; Hartshorn and Wallis, 1964; Banthorpe and Wittaker, 1966; Mori, 1976). Components identified: 1, 2, 3, *cis*-3-pinen-2-ol (4), *trans*-pinocarveol (5), nopinone (6), *trans*-verbenol (7), pinocarvone (8), myrentol (9), verbenone (10), bornyl acetate (11).

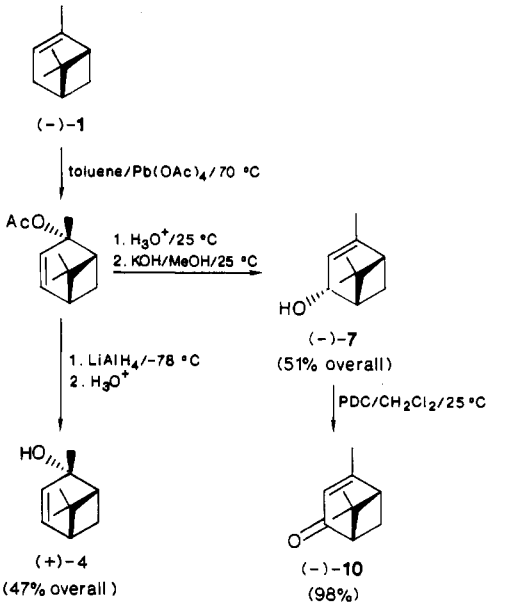
The chemistry utilized to prepare the authentic samples was generally uneventful, with the exception of the ozonolysis of 2. When 2 was treated with ozone at −78 °C in $CH_2Cl_2$ and then excess dimethyl sulfide added in the normal manner (Pappas et al., 1966), the ozonide was not

**Table I. Previously Identified Monoterpenes of *G. sarothrae*[a]**

| component | % compn | component | % compn |
|---|---|---|---|
| α-pinene[b] | 1.3 | *cis*-verbenol[b] | 1.7 |
| myrcene[b] | 1.4 | *trans*-verbenol[b,c] | 6.0 |
| linalool[b] | 1.4 | verbenone[b] | 4.2 |
| | | geraniol[b] | 53.8 |

[a] Adapted from Molyneux et al. (1980). Sample collected early spring, in New Mexico. [b] Identified by mass spectra and GLC retention time. [c] Identified by NMR and IR spectra.

**Scheme I**




**Scheme II**

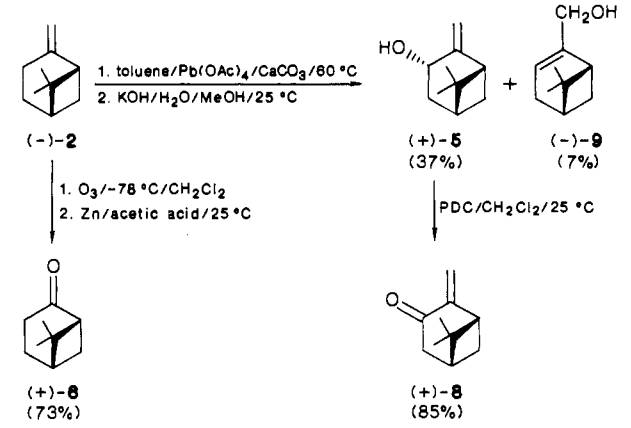



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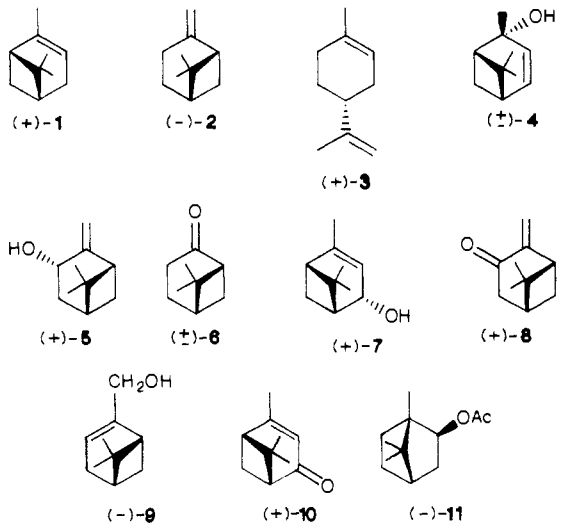
**Table II. Percentage of Monoterpenes Present in *G. sarothrae*[a,b]**

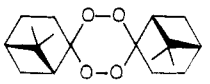
| sample (% yield oil, based on sample dry wt) | component 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | total |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| whole green plant, fall 1983 (2.07%) | 12.6 | 31.8 | 8.8 | 1.9 | 2.0 | 7.1 | 3.2 | 3.8 | 7.5 | 2.7 | 1.9 | 83.3 |
| whole green plant, fall 1984 (1.56%) | 12.6 | 28.1 | 7.2 | T | 3.8 | 10.9 | 4.6 | 2.1 | 11.3 | 6.0 | 2.1 | 88.7 |
| whole green plant, spring 1986 (2.70%) | 22.9 | 34.0 | 11.7 | T | T | 0.7 | T | 0.7 | T | T | 1.9 | 71.9 |
| whole green plant, fall 1986 (1.30%) | 14.8 | 30.7 | 10.4 | T | 1.5 | 5.7 | 2.7 | 2.1 | 5.6 | 2.7 | 1.7 | 77.9 |
| whole green plant, steam distilln, fall 1986 (1.24%) | 12.7 | 27.6 | 10.7 | T | 2.1 | 7.7 | 1.0 | 1.6 | 7.9 | 3.8 | 2.0 | 77.1 |
| whole green plant, spring 1987 (1.29%) | 22.8 | 40.4 | 11.5 | T | T | 1.3 | 0.5 | 0.8 | 0.9 | T | 1.6 | 79.8 |
| whole green plant, steam distilln, spring 1987 (1.38%) | 21.7 | 37.3 | 13.1 | T | T | 1.5 | 0.5 | 1.2 | 1.7 | 0.8 | 1.6 | 79.4 |

[a] T = trace, less than 0.5%. [b] Values are reported as percentage composition, based on GLC determinations.

**Chart I**




decomposed. Instead, the major product isolated was the known bisperoxide **12** (Overton and Owen, 1973).



**12**

Although compound **12** has been previously identified as a component of the normal ozonolysis of **2**, it is reported to be only a minor component (1.5–2.6%). While the bisperoxide was not decomposed by dimethyl sulfide, zinc and acetic acid allowed its decomposition to **6** in good overall yield (Scheme II).

The preparation of **8** and **10** involves an oxidation, and the substitution of pyridinium dichromate as the oxidant led to excellent yields (85% and 98%, respectively). A slight variation in the acetylation reaction (acetyl chloride and triethylamine) compared to the literature conditions resulted in a 95% yield of **11**.

Once the authentic samples had been purchased or prepared, and the identities of the components established, the percentages of components present in the oils were determined by capillary GLC coinjection studies (Table II). The results indicated that the nonoxygenated monoterpenes **1–3** were major components, comprising a total of 53.2% of the whole green plant oil. Whole green plant extracts of *G. sarothrae* obtained from the study site in October 1984 and 1986 give analyses nearly identical with that of the sample obtained in 1983. The combined percentage compositions of **1–3** in the oils were 47.9% and 55.9%, respectively (Table II).

The differences in the monoterpene components identified in this study and those identified previously are likely a result of subspecies variation in *G. sarothrae*. This rationalization seems highly probable, as *G. sarothrae* is an extremely variable taxon that possibly should be subdivided into a number of taxonomic varieties (Lane, 1985). The variability in both *G. sarothrae* and the components found in *G. sarothrae* suggests that the reported physiological activity is a result of only certain subspecies producing an active agent(s). This hypothesis helps to explain the observed variability of the toxic effects of *G. sarothrae*.

Although the variability between the Utah sample and the previous sample collected in New Mexico was probably due to subspecies variation, the New Mexico sample was obtained in early spring. To assure that the differences between the two studies were not due to seasonal variation, samples were collected from the Utah site in early spring, as the plants were beginning to green. The whole green plants were extracted and distilled as before to obtain oils, which were analyzed by capillary GLC coinjection studies. The same 11 components were present, but the concentrations of **1–3** (68.6% and 74.7% of the oil) were greatly increased relative to the oxygenated derivatives, while the yield of oil obtained versus dry weight of material extracted was similar to that of previous samples (Table II).

The differences in the ratios of **1–3** relative to the oxygenated components may be attributable to volatility differences resulting in the loss of the more volatile components in the later, hotter portion of the year. One might also argue that the enzymes producing the oxygenated derivatives become more active in the later part of the year, or the later stages of a plant's life cycle. Alternately, catabolism may be occurring (Croteau, 1987). All of these suggestions may be in operation, but conversion of **1** to **7**, **9**, and **10** in greater quantities in the fall would account for the larger variance of **1** between seasons, when compared to **2** and **3** (Table II). (The average variance of **1** between the fall and spring was 26.4%, while **2** and **3** varied on average by 10.4% and 13.7%, respectively.)

Because the Utah sample of *G. sarothrae* appears to be a reasonable source of **1–3**, samples were steam-distilled to show the ease of isolation of the components in yields similar to those obtained by pentane extractions (Table II).

In summary, the 11 major monoterpene components of *G. sarothrae* comprising 71.9–88.7% of the volatile oil have been identified and found to be substantially different from those previously reported. These differences are likely a result of subspecies variation although soil composition could be a factor. The chemical variation demonstrated between this study and the previous study is an indirect explanation for the variable physiological response of livestock toward *G. sarothrae*.

## EXPERIMENTAL SECTION

IR spectra were obtained on a Perkin-Elmer 298 or Bio-Rad (Digalab) FTS-40 spectrophotometer with absorbances reported in wavenumbers ($cm^{-1}$) and relative intensities reported as strong (s) (0–33% transmittance), medium (m) (34–66% transmittance), or weak (w) (67–100% transmittance). $^1H$ NMR spectra were recorded on a Varian EM-390 or XL-300 spectrometer. $^{13}C$ NMR spectra were recorded on a Varian XL-300 spectrometer. Chemical shifts are given in parts per million (ppm) relative to tetra-

methylsilane ($\delta$ 0) as internal reference. Mass spectrometric (MS) determinations were carried out on a VG Analytical 7070E double-focusing mass spectrometer at 70 eV with values reported as $m/z$ (relative intensity). A Hewlett-Packard Model HP5840A gas chromatograph with a 5 m × 2 mm (i.d.) column (Tween 80 (9%) on silanized, acid- and base-washed 100–120-mesh diatomaceous earth) was interfaced to the mass spectrometer for obtaining GLC–MS spectra. Optical rotations were measured at the 589 nm (D) line of sodium at ambient temperatures on a Perkin-Elmer 141 or 241 MC polarimeter using a 1-dm microcell with concentrations (c) expressed in grams of solute per 100 mL of solution. Melting points were obtained on a Mel-Temp melting point apparatus and are uncorrected. A Varian Series 3400 gas chromatograph with a flame-ionization detector and Varian Vista Series 420 data station were used for GLC analysis and coinjection studies, with a 30 m × 0.32 mm (i.d.) fused silica DB-5 (1-$\mu$m-thick coating) capillary column and a temperature program of 80–160 °C at 2 °C/min and then up to 250 °C at 5 °C/min. Preparative GLC was performed on a Varian Aerograph A-90-P chromatograph with a thermal conductivity detector using a 5 m × 4 mm (i.d.) Tween 80 (6%) on silanized, acid- and base-washed 80–100-mesh diatomaceous earth column. Flash chromatography was performed on 230–400-mesh ASTM silica gel 60 (EM reagents). Medium-pressure liquid chromatography (MPLC) was performed on 230–400-mesh ASTM silica gel 60 (EM reagents) with a Milton Roy minipump and Altex columns. Ethyl acetate (EtOAc) and hexanes (Hex) were distilled prior to MPLC use and spectral-grade solvents used for spectroscopic measurements. Tetrahydrofuran (THF), ether, and toluene were freshly distilled from potassium–benzophenone ketal. Dichloromethane ($CH_2Cl_2$) was freshly distilled from calcium hydride. All reagents were used as received from the chemical supplier. Reactions were run under nitrogen atmospheres unless noted otherwise. *G. sarothrae* samples were collected above the USDA station in Muskrat Canyon on the west side of the Stansbury mountains in Utah (section 20, T2S, R7W, elevation 5200–5300 ft above sea level). Fall samples were collected during mid-October, and spring samples were collected mid-May.

**Extraction of *G. sarothrae* (Fall 1983).** Green stems, leaves, and flowers (385.6 g) were ground to a fine powder at −196 °C and continuously extracted with pentanes (2 L) for 7 days. The extract was concentrated in vacuo at 0 °C to give 44.0 g (11.4% dry weight) of crude oil. Bulb to bulb distillation of the crude oil at 95 °C (0.003 Torr) gave 4.09 g (1.06% dry weight) of a clear oil. The remaining crude oil was nonequilibrium distilled at 125 °C (0.003 Torr) to give 3.88 g (1.01% dry weight) of a light yellow oil. The distilled oils were combined to give 7.97 g (2.07% dry weight) of oil, which was subjected to GLC and GLC–MS analysis. The oil was divided into 10 fractions by MPLC on a 2.5 × 1500 cm column with 10% (v/v) EtOAc/Hex as eluant. The fractions were concentrated in vacuo and then further purified by preparative GLC to give the following compounds:

*α-Pinene* (*1*): isolated as a colorless oil; $[\alpha]_D$ +4.78 (*c* 1.05, $CHCl_3$); IR (neat) 3010 m, 1380 m, 1363 m, 1655 w, 788 s; $^1H$ NMR ($CDCl_3$) 0.83 (s, 3 H), 1.12 (d, $J$ = 8 Hz, 1 H), 1.26 (s, 3 H), 1.63 (d, $J$ = 2.5 Hz, 3 H), 1.80–2.44 (m, 5 H), 5.16 (m, 1 H); MS, 136 (3), 121 (12), 93 (100), 92 (27), 91 (21), 79 (19), 77 (21), 41 (16).

*β-Pinene* (*2*): isolated as a colorless oil; $[\alpha]_D$ −12.85 (*c* 1.91, $CHCl_3$); IR (neat) 3065 m, 1638 m, 1380 m, 1365 m, 873 s, 855 m; $^1H$ NMR ($CDCl_3$) 0.71 (s, 3 H), 1.23 (s, 3 H), 1.30–2.55 (m, 8 H), 4.58 (m, 2 H); MS, 136 (5), 121 (10), 94 (13), 93 (100), 91 (14), 79 (18), 77 (19), 69 (43), 41 (52).

*Limonene* (*3*): isolated as a colorless oil; $[\alpha]_D$ +88.3 (*c* 0.74, $CHCl_3$); IR (neat) 3070 w, 1642 m, 915 m, 888 s, 798 m; $^1H$ NMR ($CDCl_3$) 1.63 (s, 3 H), 1.71 (s, 3 H), 1.15–2.23 (m, 7 H), 4.67 (s, 2 H), 5.38 (m, 1 H); MS, 136 (9), 121 (14), 107 (12), 94 (16), 93 (48), 92 (14), 91 (10), 79 (19), 77 (12), 68 (100), 67 (39), 53 (22), 41 (22).

*cis-3-Pinen-2-ol* (*4*): isolated as a colorless oil; $[\alpha]_D$ 0.0 (*c* 0.32, $CHCl_3$); IR (neat) 3580–3080 s, 3042 m, 3030 m, 1623 w, 1381 m, 1367 s, 1087 s, 907 s, 730 s; $^1H$ NMR ($CDCl_3$) 0.98 (s, 3 H), 1.34 (s, 3 H), 1.39 (s, 3 H), 1.48 (d, $J$ = 9.31 Hz, 1 H), 1.74 (s, 1 H), 2.04–2.11 (m, 1 H), 2.19–2.28 (m, 1 H), 2.39–2.48 (m, 1 H), 5.54 (dd, $J$ = 3.0, 10.0 Hz, 1 H), 6.29 (dd, $J$ = 6.4, 6.6 Hz, 1 H); $^{13}C$ NMR ($CDCl_3$) 24.01, 25.68, 27.35, 33.17, 42.55, 46.78, 53.80, 74.03, 129.79, 137.80; MS, 152 (3), 134 (8), 119 (16), 109 (16), 94 (17), 93 (100), 91 (25), 77 (10), 69 (12), 55 (11), 43 (34), 41 (23), 40 (28), 39 (11).

*trans-Pinocarveol* (*5*): isolated as a colorless oil; $[\alpha]_D$ +49.97 (*c* 1.43, $CHCl_3$); IR (neat) 3600–3100 s, 3070 m, 1645 m, 1020 s, 998 s, 890 s; $^1H$ NMR ($CDCl_3$) 0.64 (s, 3 H), 1.27 (s, 3 H), 1.62–2.68 (m, 7 H), 4.44 (d, $J$ = 8 Hz, 1 H), 4.85 (s, 1 H), 5.04 (s, 1 H); MS, 152 (1), 134 (44), 109 (32), 92 (100), 91 (59), 83 (81), 81 (34), 70 (90), 69 (48), 55 (76), 41 (79).

*Nopinone* (*6*): isolated as a colorless oil; $[\alpha]_D$ 0.0 (*c* 0.22, $CHCl_3$); IR (neat) 2951 s, 1715 s, 1387 m, 1371 m; $^1H$ NMR ($CDCl_3$) 0.85 (s, 3 H), 1.32 (s, 3 H), 1.58 (d, $J$ = 9.76 Hz, 1 H), 1.87–2.11 (m, 2 H), 2.20–2.30 (m, 2 H), 2.47–2.66 (m, 3 H); $^{13}C$ NMR ($CDCl_3$) 21.15, 21.88, 24.99, 25.66, 32.54, 40.14, 40.95, 57.69, 214.56; MS, 138 (10), 123 (7), 109 (10), 96 (10), 95 (14), 83 (100), 81 (31), 55 (32), 41 (30).

*trans-Verbenol* (*7*): isolated as a colorless oil; $[\alpha]_D$ +7.88 (*c* 0.33, $CHCl_3$); IR (neat) 3600–3050 s, 1657 w, 1380 m, 1365 m, 1022 s, 995 s, 820 m; $^1H$ NMR ($CDCl_3$) 0.87 (s, 3 H), 1.25 (s, 1 H), 1.33 (s, 3 H), 1.69 (d, $J$ = 2 Hz, 3 H), 1.82–2.35 (m, 4 H), 4.22 (m, 1 H), 5.30 (m, 1 H); MS, 152 (2), 119 (6), 109 (6), 94 (14), 93 (100), 91 (9), 43 (56).

*Pinocarvone* (*8*): isolated as a colorless oil; $[\alpha]_D$ +0.73 (*c* 0.23, $CHCl_3$); IR (neat) 1705 s, 1625 s, 922 s; $^1H$ NMR ($CDCl_3$) 0.80 (s, 3 H), 1.36 (s, 3 H), 1.70–3.10 (m, 6 H), 4.95 (d, $J$ = 2 Hz, 1 H), 5.91 (d, $J$ = 2 Hz, 1 H); MS, 150 (20), 135 (12), 108 (80), 107 (18), 81 (94), 79 (17), 69 (17), 53 (100), 43 (10), 41 (33), 40 (21), 39 (15).

*Myrentol* (*9*): isolated as a colorless oil; $[\alpha]_D$ −35.3 (*c* 0.34, $CHCl_3$); IR (neat) 3600–3000 s, 1650 w, 1378 m, 1363 m, 1143 w, 896 m; $^1H$ NMR ($CDCl_3$) 0.82 (s, 3 H), 0.9–2.53 (m, 6 H), 1.27 (s, 3 H), 3.95 (m, 2 H), 5.43 (m, 1 H); MS, 152 (3), 121 (7), 119 (10), 108 (41), 93 (27), 91 (61), 79 (100).

*Verbenone* (*10*): isolated as a colorless oil; $[\alpha]_D$ +10.0 (*c* 0.13, $CHCl_3$); IR (neat) 1670 s, 1615 m, 857 s, 814 w; $^1H$ NMR ($CDCl_3$) 1.02 (s, 3 H), 1.48 (s, 3 H), 2.01 (d, $J$ = 1.5 Hz, 3 H), 2.29–2.94 (m, 4 H), 5.67 (m, 1 H); MS, 150 (14), 135 (16), 107 (19), 91 (16), 70 (15), 43 (19), 41 (28), 40 (100), 39 (18).

*Bornyl acetate* (*11*): isolated as a colorless oil; $[\alpha]_D$ −38.14 (*c* 0.22, $CHCl_3$); IR (neat) 2957 s, 1740 s, 1381 m, 1370 m, 1248 s, 1049 s, 1034 s; $^1H$ NMR ($CDCl_3$) 0.82 (s, 3 H), 0.86 (s, 3 H), 0.89 (s, 3 H), 0.95–1.97 (m, 6 H), 2.01 (s, 3 H), 2.09–2.53 (m, 1 H), 4.85 (dd, $J$ = 2, 10 Hz, 1 H); MS, 196 (4), 136 (48), 121 (38), 95 (100), 93 (43), 43 (62).

**Extraction of *G. sarothrae* (Fall 1984).** Green stems, leaves, and flowers (1272.0 g) were treated as before to give 19.77 g (1.56% dry weight) of oil, which was subjected to GLC analysis.

**Extraction of *G. sarothrae* (Spring 1986).** Green stems, leaves, and flowers (245.0 g) were treated as before to give 6.62 g (2.70% dry weight) of oil, which was subjected to GLC analysis.

**Extraction of *G. sarothrae* (Fall 1986).** Green stems, leaves, and flowers (760.0 g) were treated as before to give 9.90 g (1.30% dry weight) of oil, which was subjected to GLC analysis.

**Steam Distillation of *G. sarothrae* (Fall 1986).** Green stems, leaves, and flowers (540.0 g) were ground to a fine powder at −196 °C and steam-distilled until 3 L of distillate was collected. The distillate was extracted with ether (3 × 350 mL). The combined ether extracts were washed with brine (250 mL), dried over $Na_2SO_4$, and concentrated in vacuo at 0 °C to give 6.70 g (1.24% dry weight) of a light yellow oil, which was subjected to GLC analysis.

**Extraction of *G. sarothrae* (Spring 1987).** Green stems, leaves, and flowers (763.0 g) were treated as before to give 9.88 g (1.29% dry weight) of oil, which was subjected to GLC analysis.

**Steam Distillation of *G. sarothrae* (Spring 1987).** Green stems, leaves, and flowers (2.0 kg) were ground to a fine powder at −196 °C and steam-distilled until 8 L of distillate was collected. The distillate was extracted with a total of 2 L of ether. The combined ether extracts were dried over $Na_2SO_4$ and concentrated in vacuo at 0 °C to give 27.5 g (1.38% dry weight) of a light yellow oil, which was subjected to GLC analysis.

(+)-*cis-3-Pinen-2-ol* (*4*): prepared by the standard literature procedure (Whitham, 1961); 1.43 g (47%) of (+)-4 as white needles; mp 44–45 °C; lit. mp 47–49 °C (Ohloff and Klein, 1962); $[\alpha]_D$ +91.41 (*c* 16.7, $CHCl_3$); lit. $[\alpha]_D$ +99.2 (*c* 3.2, $CHCl_3$). The IR, $^1H$ NMR, $^{13}C$ NMR, and MS were identical with those reported for the natural product.

(−)-*trans-Pinocarveol* (**5**) *and* (−)-*myrentol* (**9**) were prepared by the standard literature procedure (Hartshorn and Wallis, 1964). (+)-**5**: 2.13 g (37%) as a clear oil; $[\alpha]_D$ +56.87 (*c* 21.0, $CHCl_3$); lit. $[\alpha]_D$ −73.4 (*c* 5, ethanol) (Schmidt, 1949). (−)-**9**: 0.42 g (7%) as a clear oil; $[\alpha]_D$ −41.07 (*c* 18.7, ethanol); lit. $[\alpha]_D$ −45.8 (*c* 2, ethanol) (Couchman et al., 1964). The IR, $^1H$ NMR, and MS were identical with those reported for the natural products.

(+)-*Nopinone* (**6**). To a stirred solution of 1.36 g (1.58 mL, 10.0 mmol) of (1*S*)-(−)-**2** ($[\alpha]^{20}_D$ −21 (neat)) (Aldrich) in 20 mL of $CH_2Cl_2$ at −78 °C was bubbled $O_3$ until a strong blue solution was observed. The solution was purged with $N_2$ until the color discharged, and 3.11 g (3.67 mL, 50.0 mmol) of dimethyl sulfide added. The solution was warmed to room temperature, stirred overnight, concentrated in vacuo, and purified by MPLC on a 5 × 50 cm column with 15% (v/v) EtOAc/Hex to give 1.46 g of the bisperoxide **12** and 0.18 g of nopinone. The bisperoxide was characterized as follows: IR (neat) 2990 s, 2936 s, 2873 s, 1385 m, 1368 m, 1092 s, 1060 s; $^1H$ NMR ($CDCl_3$) 0.83 (s, 3 H), 1.31 (s, 3 H), 1.42–2.83 (m, 8 H). The bisperoxide was decomposed by stirring overnight in a solution of 0.8 g (12.2 mmol) of zinc dust and 4 mL of acetic acid in 10 mL of ether. The solution was diluted with water (10 mL) and extracted with ether (3 × 10 mL). The combined ether extracts were washed with water (2 × 10 mL), saturated aqueous $NaHCO_3$ (2 × 10 mL) and brine (10 mL), dried over $MgSO_4$, and concentrated in vacuo. Purification by MPLC on a 2.5 × 50 cm column using 20% (v/v) EtOAc/Hex gave 0.83 g of nopinone as a clear oil. A total of 1.01 g (73%) of nopinone was obtained: $[\alpha]_D$ +10.34 (*c* 11.9, ether); lit. $[\alpha]_D$ +38.04 (ethanol) (Wallach, 1907). The IR, $^1H$ NMR, $^{13}C$ NMR, and MS were identical with those reported for the natural product.

(−)-*trans-Verbenol* (**7**): prepared by the standard literature procedure (Whitham, 1961; Mori, 1976); 1.57 g (51%) of (−)-**7** as a clear oil; $[\alpha]_D$ −130.00 (*c* 14.3, $CHCl_3$); lit. $[\alpha]_D$ +141 ($CHCl_3$) (Mori, 1976). The IR, $^1H$ NMR, and MS were identical with those reported for the natural product.

(+)-*Pinocarvone* (**8**). To a stirred solution of 1.00 g (6.48 mmol) of (+)-**5** in 50 mL of $CH_2Cl_2$ were added diatomaceous earth (equal in volume to 4.88 g of pyridinium dichromate (PDC)) and 2.44 g (6.48 mmol) of PDC. The reaction mixture was stirred at room temperature for 1 h, 2.44 g (6.48 mmol) of PDC added, and the mixture stirred for an additional 8 h. The reaction mixture was diluted with ether (50 mL), passed through a 5 × 10 cm column of Florisil with ether as eluant, and concentrated in vacuo. Purification by MPLC on a 2.5 × 50 cm column using 10% (v/v) EtOAc/Hex gave 0.84 g (85%) of (+)-**8** as a clear oil: $[\alpha]_D$ +42.97 (neat); lit. $[\alpha]_D$ −69.2 (neat) (Schmidt, 1944). The IR, $^1H$ NMR, and MS were identical with those reported for the natural product.

(−)-*Verbenone* (**10**). A stirred solution of 0.50 g (3.24 mmol) of (−)-**7** in 25 mL of $CH_2Cl_2$ was treated in an analogous manner as for the preparation of **8** using 2.44 g of PDC to give 0.48 g (98%) of (−)-verbenone as a clear oil: $[\alpha]_D$ −242.34 (*c* 18.6, $CHCl_3$); lit. $[\alpha]_D$ +282 (calculated) (Banthorpe and Wittaker, 1966). The IR, $^1H$ NMR, and MS were identical with those reported for the natural product.

*Bornyl Acetate* (**11**). To a stirred solution of 2.00 g (13.0 mmol) of borneol (Aldrich) and 1.98 g (2.73 mL, 19.4 mmol) of triethylamine in 15 mL of ether at 0 °C was added dropwise 1.22 g (1.11 mL, 15.6 mmol) of acetyl chloride. The reaction mixture was stirred 15 min, diluted with water (10 mL), and extracted with ether (2 × 15 mL). The combined ether extracts were washed with water (10 mL), saturated aqueous $NaHCO_3$ (10 mL), and brine (10 mL), dried over $MgSO_4$, and concentrated in vacuo. Purification by MPLC on a 2.5 × 50 cm column using 10% (v/v) EtOAc/Hex gave 2.42 g (95%) of **11** as a clear oil. The IR, $^1H$ NMR, and MS were identical with those reported for the natural product.

## LITERATURE CITED

Banthorpe, D. V.; Wittaker, D. The Preparation and Stereochemistry of Pinane Derivatives. *Chem. Rev.* **1966**, *66*, 643–56.

Couchman, F. M.; Pinder, A. R.; Bromham, N. M. Studies on the Essential Oil of *Cyprus Articulatus* L. *Tetrahedron* **1964**, *20*, 2037–45.

Croteau, R. Biosynthesis and Catabolism of Monoterpenoids. *Chem. Rev.* **1987**, *87*, 929–54, and references therein.

Hartshorn, M. P.; Wallis, A. F. A. Some Addition Reactions of β-Pinene Derivatives. *J. Chem. Soc.* **1964**, 5254–60.

Kingsbury, J. M. *Poisonous Plants of the United States and Canada*; Prentice-Hall: Englewood Cliffs, NJ, 1964; pp 406–9, and references therein.

Lane, M. A. Taxonomy of *Gutierrezia* (Compositae: *Astereae*) in North America. *Syst. Biol.* **1985**, *10*, 7–28.

Molyneux, R. J.; Stevens, K. L.; James, L. F. Chemistry of Toxic Range Plants. Volatile Constituents of Broomweed (*Gutierrezia Sarothrae*). *J. Agric. Food Chem.* **1980**, *28*, 1332–33.

Mori, K. Synthesis of Optically Pure (+)-*trans*-Verbenol and its Antipode, The Phenomone of *Dendroctonus* Bark Beetles. *Agric. Biol. Chem.* **1976**, *40*, 415–18.

Ohloff, G.; Klein, E. Die Absolute Konfiguration Des Linalools Durch Verknüpfung mit dem Pinansystem. *Tetrahedron* **1962**, *18*, 37–42.

Overton, K. M.; Owen, P. Bis-(6,6-dimethylnorpinane-2,2-diyl)-Diperoxide. *J. Chem. Soc., Perkin Trans. 1* **1973**, 226–27.

Pappas, J. J.; Keaveney, W. P.; Gancher, E.; Berger, M. A New Method for Converting Olefins to Aldehydes. *Tetrahedron Lett.* **1966**, 4273–78.

*Range Plant Handbook*; Forrest Service, USDA: Washington, DC, 1937; p 419.

Schmidt, H. Zur Ramuisomerie in der Pinanreihe, IV. Mitteil: Pinocarvon und die Beiden Diastereomeren Pinocarveole. *Chem. Ber.* **1944**, *77*, 167–72.

Wallach, O. Zur Kenntniss der Terpene und der ätherischen Oele. *Leibigs Ann. Chem.* **1907**, *356*, 227–49.

Whitham, G. H. The Reaction of α-Pinene with Lead Tetra-Acetate. *J. Chem. Soc.* **1961**, 2232–36.

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